



Indiana Department of Environmental Management
Office of Land Quality
100 N. Senate
Indianapolis, IN 46204-2251
OLQ PH: (317) 232-8941

GUIDANCE

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Determining the Fraction of Organic Carbon RISC Nondefault Option

Background

Soil can be a complex mixture of mineral-derived compounds and organic matter. The ratios of each component can vary widely depending on the type of soil being investigated. Soil organic matter is a term used by agronomists for the total organic portion of the soil and is derived from decomposed plant matter, microorganisms, and animal residues. The decomposition process can create complex high molecular weight biopolymers (e.g., humic acid) as well as simpler organic compounds (decomposed lignin or cellulose). Only the simpler organic compounds contribute to the fraction of organic carbon.

There is not a rigorous definition of the fraction of organic carbon (*Foc*). However, it can be thought of as the portion of the organic matter that is available to adsorb the organic contaminants of concern. The higher the organic carbon content, the more organic chemicals may be adsorbed to the soil and the less of those chemicals will be available to leach to the ground water. A nondefault option in the Risk Integrated System of Closure (RISC) is to use *Foc* in the Soil to Ground Water Partitioning Model to calculate a site specific migration to ground water closure level. In the Soil to Ground Water Partition Model, the coefficient, K_d , for organic compounds is the *Foc* multiplied by the chemical-specific soil organic carbon water partition coefficient, K_{oc} . Therefore for organic compounds,

$$K_d = Foc \times K_{oc}$$

Typical Indiana surface soils have soil organic matter (SOM) contents in the 1 – 6% range, depending upon soil type. Since organic carbon is thought to comprise about 58% of the SOM, the upper range of *Foc* for fertile surface soil is expected to be less than approximately: 6% SOM * 0.58 = 3.42% (0.0342 g/g) organic carbon. Subsurface soils are expected to be much lower in organic matter. The EPA's Soil Screening Guidance recommends 0.2% (0.002 g/g) as the default concentration of organic carbon for subsurface soils. *Foc* concentrations above the RISC default concentration of 0.2% (0.002 g/g) will necessitate an explanation of the source of the organic carbon being reported.

The use of *Foc* as a nondefault option is considered a background condition. Therefore, samples from four borings should be collected from an area unaffected by the unit or facility, i.e., not in a contaminated area. Samples must be taken from the same types of soil or strata that are at, and below, the contaminated soil. Analyze each sample in triplicate. The *Foc* for the site is the mean of all the samples. Submitted results should include boring locations and boring logs, and the soil series and map unit from the USDA County Soil Survey. As with any nondefault proposal,

results are subject to IDEM approval. **Samples should also be analyzed for the contaminants of concern to demonstrate that the *Foc* samples are not contaminated.**

Sample Handling and Pretreatment

There should be no extraneous organic matter in the sample, e.g., roots, sticks, wood, paper, or biota. Samples should be air-dried and large chunks of sample pulverized to pass through a Number 10 (2 mm) sieve.

Indiana soils derived from glacial till are calcareous and require pretreatment to remove the inorganic carbon prior to analysis. For the dichromate oxidation methods, this can be done by addition of an acid to the soil sample. HCl should be avoided because it introduces Cl⁻, an interferent. A suitable pretreatment acid is a combination of H₂SO₄ and FeSO₄ (Schumacher, 2002; Nelson and Sommers, 1996).

Analytical Methods for *Foc*

There are two approaches commonly used, the dichromate oxidation method (commonly referred to as Walkley-Black) and the loss on ignition method (ASTM 2974-00 D). The ASTM method is not appropriate for environmental remediation purposes. The dichromate oxidation method is, however, appropriate for determining the low concentrations of organic carbon expected in Indiana subsurface soils.

While specialized equipment for high temperature dry combustion, (which capture and quantitate the evolved CO₂), are widely accepted in the soil literature, consult with IDEM before using such a method. Note, EPA Method SW 846-9060A TOC and EPA Method MCAWW-415.1 are water methods and are not acceptable for determining organic carbon in soil.

Dichromate Oxidation Method (Walkley-Black)

The Walkley-Black method is most appropriate for subsurface soil samples in Indiana. This wet chemistry technique can be divided into two phases, sample extraction (oxidation) and sample quantitation. There are two basic variations on the basic dichromate oxidation (extraction) of the sample. The basic Walkley-Black oxidation relies upon the heat of solution of the sulfuric acid and water for the reaction. This method incompletely oxidizes the organic carbon and a correction factor of 1.3 is commonly applied to the results to adjust the easily oxidizable carbon to total organic carbon. The second variation entails heating the reaction mixture for a specified time period to achieve complete oxidation of the organic carbon. No correction factor is needed for this variation. (Mebius, 1960; Tinsley, 1950; Kalembasa & Jenkinson, 1973; and others).

The unreacted dichromate should be determined by titration with ferrous ammonium sulfate to a potentiometric endpoint with an automated titrator. An acceptable alternative to titration is the spectrophotometric method described by Sims & Haby, 1971. Specific details on acceptable methods are found in the following references at the end of this guidance. Manual titration to the color change endpoint is less precise and not recommended. Consult with IDEM's OLQ Chemistry staff if you have any questions about particular methods and details.

Due to the small amount of soil used in each analysis, each sample should be analyzed in triplicate to obtain an estimate of how precise the measurement is. A reagent blank should be prepared and analyzed along with each sample set. Laboratory control spike/spike duplicates should be analyzed with each analytical batch of 20 or fewer samples. Standard reference

materials should be analyzed along with the samples. In addition, the percent moisture should be determined from a separate sample and the results reported on a dry weight basis.

Documentation Requirements

The General Sampling Quality Control Data and Information, and the General Laboratory Quality Control Data and Information requirements in Appendix 2 of the RISC Technical Guide should be followed. The specific method should be cited as well as details of the analytical procedures. Because there may be procedural variations among laboratories, a copy of the laboratory's SOP for the method should be submitted with the data package. The data package must include the boring logs and soil type as described in the USDA County Soil Survey.

Deliverables

Sample Deliverables

- Chain of Custody Noting Date and Time of Sampling
- Map with Boring Location
- Geographic Coordinates Determined by GPS for Each Boring
- Boring Logs with USDA Soil Classifications (for comparing both investigative samples and *Foc* samples)
- Number and Depth of Soil Strata

Analytical Deliverables

- Laboratory SOP
- Laboratory Internal Chain of Custody
- Sample Identification
- Laboratory Reagents and Standards
- Sample pre-treatment and/or particle size reduction
- Date and Time of Analysis
- Lab Sheets Showing
 - Weight of sample
 - Volume and Normality (or Molarity) of Dichromate Solution
 - Volume and Normality (or Molarity) of Titrant
 - Reaction Time
 - Temperature of Reaction (if reaction is heated)
- Calibration Results (appropriate for determinative method)
- Blank Results Determining Concentration of Titrant
- Laboratory Control Samples and Duplicate Results
- Moisture Content of Soil Samples
- Average of Each *Foc* Sample (triplicate analyses) in Dry Weight
- Percent Relative Standard Deviation (% RSD) of Triplicate Analyses
- Average *Foc* of Each Soil Strata

References

Burt, Rebecca, Ed. Soil Survey Laboratory Methods Manual, Natural Resources Conservation Service, Soil Survey Investigations Report No. 42, Version 4.0, November 2004.

Mebius, L.J. 1960. A Rapid Method for the Determination of Organic Carbon in Soil. *Anal Chim. Acta.* 22:120-124.

Kalmebasa, S.J., and D.S. Jenkinson, 1973. A Comparative Study of Titrimetric and Gravimetric Methods for the Determination of Organic Carbon in Soil. *J. Sci. Food Agric.* 24:1085-1090.

Nelson, D.W. and Sommers, L.E. 1996. Chapter 34, Total Carbon, Organic Carbon and Organic Matter, *In* Sparks, D.L. Ed. *Methods of Soil Analysis Part 3 – Chemical Methods*. Soil Science Society of America and American Society of Agronomy, 677 S Segoe Rd, Madison, WI 53771, 1996.

Risk Integrated System of Closure, RISC, Technical Resource Guidance Document, Indiana Department of Environmental Management, February 15, 2001 and updates.

Schulte, E.E. 1995. Chapter 8 Recommended Soil Organic Matter Tests. *In* Recommended Soil Testing Procedures For The Northeastern United States, 2nd Ed., Northeastern Regional Publication No. 493. Cooperative Extension, University of Delaware College of Agriculture & Natural Resources.

Schumacher, Brian A. 2002. Methods for the determination of total organic carbon (TOC) in soils and sediments. USEPA Environmental Sciences Division National Exposure Research Laboratory, Ecological Risk Assessment Support Center, Office of Research and Development, Las Vegas, NV.

Sims, J.R. and V.A. Haby. 1971. Simplified colorimetric determination of soil organic matter. *Soil Sci.* 112:137-141.

Tinsley, J. 1950. Determination of organic carbon in soils by dichromate mixtures. P. 161-169. *In* Trans. 4th Int. Congr. Soil Sci., Vol. 1 Hoitsema Brothers, Groningen, the Netherlands.

U.S. EPA. Soil Screening Guidance: User's Guide. EPA/540/R-96/018, April 1996.

Walkley, A., and Black, I.A. 1934. An examination of the Degtijareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* 37:29-38.